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(21) International Application Number: PCT/GB90/00938 (22) International Filing Date: 18 June 1990 (18.06.90) (30) Priority data: 8914037.0 19 June 1989 (19.06.89) GB (71) Applicant (for all designated States except US): UNIVERSITY COLLEGE CARDIFF CONSULTANTS LIMITED [GB/GB]; 51 Park Place, Cardiff CF1 3AT (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : WILLIAMS, Peter, Alan [AU/GB]; 64 Cardiff Road, Dinas Powys, South Glamorgan CF6 4JX (GB). ANTHONY, Elizabeth, Youngblood [US/US]; 2320 North Virginia Road, El Paso, TX 79902 (US).		(74) Agent: NEVILLE, Peter, Warwick; Patent Department, National Research Development Corporation, 101 Newington Causeway, London SE1 6BU (GB). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), SU, US. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: DISSOLVING VALUES OF PLATINUM GROUP METALS FROM ORES AND CONCENTRATES (57) Abstract Platinum group metals are recovered from lower-grade ores than hitherto considered economic by lixiviation with aqueous arsenate or thiosulphate, plus halide, in air.		

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- 1 -

DISSOLVING VALUES OF PLATINUM GROUP METALS
FROM ORES AND CONCENTRATES

This invention relates to a method of dissolving values of platinum group metals from ores and concentrates, for subsequent treatment for recovery of the metal. The "platinum group" of metals is: ruthenium, rhodium, palladium, osmium, iridium and
05 platinum. The method is especially applicable to palladium and platinum, which are normally regarded, when in ore, as difficult to raise to an oxidation number at which they will form water-soluble compounds.

Although alluvial and other mineral deposits of platinum
10 group metals are the result of natural concentration processes involving weathering and gravity-separation phenomena, considerable additional treatment is required to yield a product suitable for marketing. After treatments which might typically include crushing, froth flotation and gravity separation, part of
15 the resultant material might be sent directly to the refinery. The remainder is concentrated further by smelting, oxygen blowing, magnetic separation, and pressure leaching (removing e.g. nickel which has been solubilised) to yield a final concentrate, a 60% residue of platinum group metals.

20 Most refining procedures take advantage of the ready solubility of platinum and palladium (and gold) in aqua regia, which does not dissolve the other platinum group metals (ruthenium, rhodium, osmium and iridium) and indeed it is conventional wisdom that only highly oxidising substances of this
25 type will dissolve elemental palladium and platinum. (US Patent 4337226 suggests H_2SO_4 plus either $NaOCl$ or H_2O_2 .) Platinum is indeed known for its property of remaining unattacked by for example hot sulphur dioxide, and functioning for years as a catalyst for oxidising that gas at $600^\circ C$. It is therefore most
30 unexpected that sulphur-oxygen compounds can be used to dissolve values of platinum group metals.

- 2 -

According to the present invention, a method of dissolving platinum group metals from ores or concentrates comprises lixiviating the ore or concentrate in the presence of an oxidant with an aqueous solution containing a material being a compound or polyelemental anion having an atom in a lower oxidation state, and which material is stable in the presence of the oxidant and can co-ordinate a platinum group cation through the said atom. A "lower oxidation state" is any non-zero oxidation state lower than the highest normally attained, which in the case of for example sulphur is taken as 6, and arsenic 5. The counter ion of the anion if present may be an alkaline earth or alkali metal, conveniently sodium. The solution is preferably at least $10^{-4}M$ in said atom, preferably at least $10^{-3}M$, most preferably at least $10^{-2}M$, and usefully at least $0.04M$. It is preferably under $1M$, more preferably under $\frac{1}{2}M$.

Examples of such materials are: $As(OH)_3$ or salts thereof; organic sulphides and thio derivatives e.g. thioketones such as thiourea H_2NCSNH_2 ; thiosulphate $S_2O_3^{--}$; dithionate $S_2O_6^{--}$ and polythionate $(O_3S-S_x-SO_3)^{--}$, and the selenium and tellurium analogues (where they exist) of these sulphur materials. As lixiviants in extractive metallurgy go, some of these are not costly and some are relatively mild environmentally.

In the case of (for example) thiosulphate, it is postulated that because the thiosulphate ion is a soft donor (via sulphur), it effectively lowers the redox potential at which the metals are oxidized. An important cooperative effect in practice is its fast rate of oxidation of the metals, especially palladium and platinum, particularly in the presence of the appropriate ligands, to form coordination complexes under ambient conditions.

- 3 -

This discovery represents a novel way of extracting platinum group elements from their ores and concentrates by a simple leaching procedure using cheap and readily available reagents. It is also the case that since bulk leaching operations are relatively inexpensive, lower grade ores than have been hitherto thought to be economic and deposits which have hitherto not been mined for their platinum group metals content could now be exploited, such as the low-grade deposits of Pt and Pd concentrated during weathering of mafic and ultramafic rocks such as in the Fifield, NSW area and in weathered sulphide ores (gossans and the like) overlying primary sulphides in certain of the deposits of the West Australian shield.

Arsenic (III) species preferably in acid solution (more preferably pH 3-4) may be used especially for mobilizing palladium.

Preferably, means are employed to inactivate microbes such as Thiobacilli which could mediate the concentrations of the lixivants during the dissolution.

Preferably other ligating anions are additionally present such as halide. Chloride is convenient, and bromide and iodide are better although in practice disproportionately more costly.

The oxidant which must be present is most conveniently oxygen in air at ambient temperature and pressure.

The duration of the lixiviation is preferably at least 7 days, more preferably at least 12 days.

The resulting solution of platinum group metal(s) is then normally separated from the residual solids, and then treated to recover the metal(s).

- 4 -

The invention will now be described by way of example.

EXAMPLE 1

A fixed mass of comminuted ore containing platinum and palladium was leached with a fixed volume of 0.001 molar aqueous sodium thiosulphate under recycling conditions at ambient temperatures (ca 20°C) in the presence of air. The pH of the solution was maintained at a fixed value above 6 (otherwise the thiosulphate would have decomposed) via the use of sodium carbonate Na_2CO_3 , sodium hydrogen carbonate NaHCO_3 , sodium hydroxide NaOH , lime CaO or Ca(OH)_2 and/or calcium carbonate CaCO_3 . The rate of dissolution of platinum and palladium was monitored from time to time by taking samples and analysing for dissolved metals with the results below. When amounts in solution were judged to be sufficient, the solution was filtered to remove solids and the dissolved values recovered by (i) oxidation of the contained thiosulphate to produce a precipitate containing the values or (ii) reduction of the values with an appropriate reducing agent e.g. zinc to precipitate the platinum group metals as a concentrate ready for further refining.

	Thiosulphate concentration	pH	Palladium Concentration in Solution	
			after 14 days	after 23 days
	0.001M	8.9	35 ppm	—
	0.01M	8.9	32 ppm	41 ppm
25	0.05M	8.5	44 ppm	56 ppm
	0.1M	8.5	70 ppm	97 ppm (32 days)

- 5 -

EXAMPLE 2

Leaching is made more effective in certain instances for certain metals by addition of auxiliary ligands. Example 1 was repeated with the additional reagent sodium chloride present in solution at a concentration of 0.01 molar. Iridium was leached from the ore.

EXAMPLE 3

Palladium was leached from a sample of ore in a manner analogous to that described above, but using (instead of thiosulphate) sodium arsenite or arsenic (III) oxide dissolved in water (0.05 molar in arsenic in either case) and which was made acid to a fixed pH below 5 with hydrochloric acid, in the presence of air at ambient temperatures. At higher values of pH, arsenic (III) can form $\text{As}(\text{OH})_4^-$, a hard ligand in which moreover the arsenic atom is "buried" and no longer available to ligate palladium. The HCl both prevented this and provided Cl^- ions as auxiliary ligands.

After 15 days in each case, the palladium concentration in the solution was measured, and compared with the result when arsenic was omitted.

	<u>pH held at</u>	<u>ppm Pd using arsenic</u>	<u>ppm Pd omitting arsenic</u>
	2	90	20
	3	175	4
25	4	16	not detectable
	5	5	not detectable

- 6 -

CLAIMS

1. A method of dissolving platinum group metals from ores or concentrates, comprising lixiviating the ore or concentrate in the presence of an oxidant with an aqueous solution containing a material being a compound or polyelemental anion having an atom
05 in a lower oxidation state as hereinbefore defined, and which material is stable in the presence of the oxidant and can co-ordinate a platinum group cation through the said atom.
2. A method according to Claim 1, wherein the counter ion of the anion is an alkaline earth or alkali metal.
- 10 3. A method according to Claim 1 or 2, wherein the aqueous solution is at least 10^{-4} M in said atom.
4. A method according to Claim 3, wherein the solution is at least 10^{-3} M in said atom.
5. A method according to Claim 4, wherein the solution is at
15 least 10^{-2} M in said atom.
6. A method according to Claim 5, wherein the solution is at least 0.04M in said atom.
7. A method according to any preceding claim, wherein the aqueous solution is under 1M in said atom.
- 20 8. A method according to Claim 7, wherein the solution is under $\frac{1}{2}$ M in said atom.
9. A method according to any preceding claim, wherein the platinum group metal is platinum and/or palladium.
10. A method according to any preceding claim, wherein the said
25 material is: $\text{As}(\text{OH})_3$ or a salt thereof; or an organic sulphide or thio derivative or its selenium or tellurium analogue.
11. A method according to any of Claims 1 to 9, wherein the said material is thiosulphate, dithionate or polythionate or its selenium or tellurium analogue.
- 30 12. A method according to Claim 10, wherein palladium is dissolved and wherein the said material is arsenic(III).
13. A method according to Claim 12, wherein the arsenic(III) is in acid solution.

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- 7 -

14. A method according to Claim 13, wherein the arsenic(III) solution has a pH of 3 to 4.

15. A method according to any preceding claim, further comprising means to inactivate microbes during the dissolution.

05 16. A method according to any preceding claim, wherein other ligating anions are additionally present.

17. A method according to Claim 16, wherein said other ligating anions comprise halide.

10 18. A method according to any preceding claim, wherein said oxidant is oxygen in the air.

19. A method according to any preceding claim, wherein the duration of the lixiviation is at least 7 days.

20. A method according to Claim 19, wherein the duration of the lixiviation is at least 12 days.

15 21. A method according to any preceding claim, further comprising separating the resulting solution of platinum group metal(s) from the residual solids.

22. A method according to Claim 21, further comprising treating the separated solution to recover the metal(s).

INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 90/00938

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC⁵: C 22 B 11/04

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

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IPC⁵ | C 22 B

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched *

III. DOCUMENTS CONSIDERED TO BE RELEVANT *

Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹²
X	US, A, 4561947 (R. SCHULZE) 31 December 1985 see claims; column 2, paragraph 5 --	1,9-10
X	GB, A, 2181452 (DEAN BUTTLER) 23 April 1987 see claims; page 2, lines 10-29 --	1-11,17
A	DE, C, 95444 (F.W. DUPRÉ) 27 November 1897 see claim --	1,11
A	US, A, 3545965 (A.L. JACOBS) 8 December 1970 see claims --	1,10
A	US, A, 4645535 (R.H. LITTLE) 24 February 1987 see claims	1-2,10

* Special categories of cited documents: ¹³

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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IV. CERTIFICATION

Date of the Actual Completion of the International Search

14th September 1990

Date of Mailing of this International Search Report

17. 10. 90

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

H. Ballesteros

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

GB 9000938
SA 37556

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 04/10/90. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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